

FERROELECTRIC THIN FILM ELEMENT, PIEZOELECTRIC
ACTUATOR AND LIQUID DISCHARGE HEAD

BACKGROUND OF THE INVENTION

5 Field of the Invention

The present invention relates to a ferroelectric thin film element, and more particularly to an element in which a spontaneous polarization of a ferroelectric thin film is involved 10 in an improvement in device characteristics, such as a non-volatile memory. The present invention also relates to a piezoelectric actuator utilizing piezoelectric property an epitaxial film and a liquid discharge head equipped with a piezoelectric actuator 15 unit of a configuration including such piezoelectric actuator.

Description of the Related Art

As a memory medium for a non-volatile memory and the like, there is recently desired a memory 20 apparatus employing a ferroelectric thin film of a high performance (hereinafter called ferroelectric memory). For securing optimal device characteristics and reproducibility in the ferroelectric memory, the ferroelectric thin film is required to have a large 25 spontaneous polarization (residual polarization), a small temperature dependence of the residual polarization, and a small deterioration of inversion

of polarization in repeated cycles.

As the ferroelectric material, lead zirconate titanate [Pb(Zr, Ti)O₃] (also represented as PZT) is principally employed. PZT is a solid solution of
5 lead zirconate and lead titanate, and a solid solution of a molar ratio of about 1:1 is considered to have a large spontaneous polarization, capable of inversion even under a weak electric field and excellent as a memory medium. As PZT has a
10 relatively high transition temperature (Curie temperature) between a ferroelectric phase and a paraelectric phase of about 300°C or higher, there is little concern that the memorized content is lost by heat in a temperature range in which ordinary
15 electronic circuits are used (120°C or lower).

However, even in an excellent ferroelectric thin film such as a PZT thin film, it is difficult to obtain satisfactory device characteristics in a ferroelectric thin film formed by a polycrystalline
20 member, because of a distortion of physical properties at the crystal grain boundary. Therefore, in consideration of device characteristics of the ferroelectric element, there is desired an epitaxial thin film as close to a complete single crystal as
25 possible.

Also for integration of the ferroelectric devices, a thinner film formation of the

ferroelectric thin film is effective, but in case a film thickness of the ferroelectric thin film becomes equal to or less than 100 nm, the spontaneous polarization of the ferroelectric thin film tends to 5 be lost even in case it is an epitaxial film, and a deterioration in the residual polarization or the fatigue resistance of the ferroelectric thin film becomes conspicuous. For this reason, in order to reduce the thickness of the ferroelectric thin film, 10 there is required certain measure for maintaining the spontaneous polarization of the ferroelectric thin film at a sufficiently large level.

In order to increase the spontaneous polarization of the ferroelectric thin film, there 15 can be employed a method of utilizing a mismatch in the thermal expansion coefficient between the substrate and the ferroelectric thin film (Japanese Patent Application Laid-Open No. H08-186182), or a method of utilizing a misfit in the lattices of the 20 substrate and the ferroelectric thin film (Japanese Patent Application Laid-Open No. H08-139292). These methods can cause a compression stress to be applied to the ferroelectric thin film, thereby increasing the spontaneous polarization of the ferroelectric 25 thin film.

However the prior method of increasing the spontaneous polarization by applying a compression

stress to the ferroelectric thin film, though capable of increasing the spontaneous polarization, cannot improve the deterioration in the residual polarization or the fatigue resistance of the
5 ferroelectric thin film. It is estimated that a stress applied in the ferroelectric thin film along a planar direction of the substrate is significantly involved in the aforementioned deterioration of the characteristics of the ferroelectric thin film, and,
10 in case a large compression stress is applied to the ferroelectric thin film in the prior method, the stress applied along the planar direction of the substrate acts on the ferroelectric thin film, thereby further enhancing the deterioration in the
15 characteristics of the ferroelectric thin film.

On the other hand, a printer utilizing an ink jet recording apparatus is widely popular as a printing apparatus for a personal computer or the like, because of a satisfactory printing ability, a
20 simple handling and a low cost. An ink jet head employed in such ink jet recording apparatus is a liquid discharge head for discharging ink, and is available in various types such as one generating a bubble in the ink by thermal energy and discharging
25 an ink droplet by a pressure wave caused by such bubble, one sucking and discharging an ink droplet by an electrostatic force, and one sucking and

discharging an ink droplet utilizing a pressure wave generated by an actuator having a vibrator such as a piezoelectric element or an electrostriction element.

- A liquid discharge head utilizing a
- 5 piezoelectric actuator generally has a pressure chamber communicating with a liquid supply chamber, and a liquid discharge port communicating with such pressure chamber, and, in a part of the pressure chamber, there is provided a vibrating plate on which
- 10 a piezoelectric actuator is adjoined or directly formed. In the liquid discharge head of such configuration, a predetermined voltage is applied to the piezoelectric actuator to cause an extension-contraction motion of the piezoelectric element,
- 15 thereby inducing a bending vibration and pressurizing the liquid in the pressure chamber to discharge a liquid droplet from the liquid discharge port.

- A color ink jet recording apparatus is currently becoming popular, and there is being
- 20 requested an improvement in the printing performance, particularly for a higher resolution and a higher printing speed. For this end, it is attempted to achieve a high resolution and a high-speed printing by a multi-nozzle head structure through a
- 25 miniaturization of the liquid discharge head for liquid discharge. For miniaturizing the liquid discharge head, it is necessary to reduce the

dimension of the piezoelectric actuator for liquid discharge.

In the piezoelectric actuator and the liquid discharge head, a compact piezoelectric actuator has 5 conventionally prepared by fine working, such as grinding and polishing, of a piezoelectric member prepared by sintering, but it is separately being investigated to develop an ultra small piezoelectric actuator of a high precision by forming a 10 piezoelectric member as a film and utilizing a fine working technology developed in the semiconductor field. Also in view of achieving a higher performance, such piezoelectric film is preferably a film having a single crystal structure or a crystal 15 orientation property, and a heteroepitaxial growing technology is being actively developed.

Also in case of employing a ferroelectric member as a piezoelectric member, a large spontaneous polarization is one of the characteristics desired 20 for the ferroelectric member. However, in case of a film, a reduction in the film thickness of the ferroelectric film tends, even in case the ferroelectric film is an epitaxial film, to lose the spontaneous polarization of the epitaxial 25 ferroelectric film, and there is required certain measure for maintaining the spontaneous polarization of the epitaxial ferroelectric film at a sufficiently

high level.

In order to increase the spontaneous polarization of the epitaxial ferroelectric film, as stated above, there can be employed a method of 5 utilizing a mismatch in the thermal expansion coefficient between the substrate and the ferroelectric film (Japanese Patent Application Laid-Open No. H08-186182), or a method of utilizing a misfit in the lattices of the substrate and the 10 ferroelectric film (Japanese Patent Application Laid-Open No. H08-139292). These methods can form an epitaxial ferroelectric film involving a compression stress therein, thereby obtaining an epitaxial ferroelectric film with a large spontaneous 15 polarization.

However the prior method of forming an epitaxial ferroelectric film involving a compression stress therein to increase the spontaneous polarization thereby improving the piezoelectric 20 property, though capable of increasing the spontaneous polarization, cannot resolve drawbacks such as a deterioration in the characteristics of the piezoelectric actuator in repeated uses or a destruction of the piezoelectric actuator induced by 25 a leak current at a voltage application. It is estimated that a stress applied in the ferroelectric thin film along a planar direction of the substrate

is significantly involved in the aforementioned deterioration in the characteristics and destruction of the piezoelectric actuator, and, in an epitaxial ferroelectric film prepared by a prior method and
5 subjected to a large compression stress, the stress applied along the planar direction of the substrate acts on the ferroelectric thin film, thereby further enhancing the deterioration in the durability characteristics of the piezoelectric actuator.

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SUMMARY OF THE INVENTION

An object of the present invention is to provide a ferroelectric thin film element which is free from deterioration of characteristics of the
15 ferroelectric thin film element because of a small stress applied in the ferroelectric thin film along a planar direction of a substrate, shows a large spontaneous polarization of the ferroelectric thin film and is suitable for a thin film formation. It
20 is effective for an element in which the spontaneous polarization of the ferroelectric thin film is involved in improving the characteristics of the ferroelectric thin film element, for example a non-volatile memory. In a heteroepitaxial growing
25 technology, it is preferable to reduce a stress generated in the vicinity of a boundary between the substrate and the formed ferroelectric thin film and

applied along the planar direction of the substrate. It is estimated that a stress generated by a misfit in the crystal lattices between the substrate and the ferroelectric thin film and applied in the planar
5 direction of the substrate constitutes a cause of a film peeling of the ferroelectric thin film, so that such film peeling can be prevented by a reduction in the aforementioned stress applied in the planar direction of the substrate.

10 Another object of the present invention is to provide a ferroelectric thin film element having a substrate and an epitaxial ferroelectric thin film provided on the substrate, in which the epitaxial ferroelectric thin film satisfies a relation $z/z_0 >$
15 1.003 wherein a crystal face parallel to a crystal face of a surface of the substrate among crystal faces of the epitaxial ferroelectric thin film is taken as a Z crystal face, a face spacing of the Z crystal face is taken as z and a space of the Z
20 crystal face of a material constituting the epitaxial ferroelectric thin film in a bulk state is taken as z_0 , and also satisfies a relation $0.997 \leq x/x_0 \leq 1.003$ wherein one of crystal faces of the epitaxial ferroelectric thin film perpendicular to the Z
25 crystal face is taken as an X crystal face, a face spacing of the X crystal face is taken as x and a face spacing of the X crystal face of the material

constituting the epitaxial ferroelectric thin film in a bulk state is taken as x_0 . According to the present invention, there can be obtained a ferroelectric thin film element free from deterioration of the
5 characteristics of the ferroelectric thin film element, showing a large spontaneous polarization and suitable for thin film formation.

Still another object of the present invention is to provide a piezoelectric actuator having
10 excellent characteristics, by forming an epitaxial ferroelectric film which is capable of reducing a stress acting on the epitaxial ferroelectric film along a planar direction of the substrate, is free from a film peeling or a deterioration in the
15 characteristics of the epitaxial ferroelectric film, enables a large area formation, has excellent piezoelectric characteristics and is suitable for a thin film formation. Also another object of the present invention is to provide a liquid discharge
20 head, particularly a liquid discharge head adapted for use in an ink jet recording apparatus, provided with a piezoelectric actuator unit of a configuration including such piezoelectric actuator. In a heteroepitaxial growing technology, it is preferable
25 to reduce a stress, generated in the vicinity of a boundary between a substrate and a formed epitaxial ferroelectric film and applied along a planar

direction of the substrate. By reducing a stress generated by a misfit in lattices of the substrate and the epitaxial ferroelectric film and applied in the planar direction of the substrate, it is rendered
5 possible to prevent a film peeling of the epitaxial ferroelectric film, thereby enabling to improve the productivity by an increase in the size of the substrate.

Still another object of the present invention
10 is to provide a piezoelectric actuator having a substrate and an epitaxial ferroelectric film provided on the substrate, in which the epitaxial ferroelectric film satisfies a relation $z/z_0 > 1.003$ wherein a crystal face parallel to a crystal face of
15 a surface of the substrate among crystal faces of the epitaxial ferroelectric film is taken as a Z crystal face, a face spacing of the X crystal face is taken as z and a space of the Z crystal face of a material constituting the epitaxial ferroelectric film in a
20 bulk state is taken as z_0 , and also satisfies a relation $0.997 \leq x/x_0 \leq 1.003$ wherein one of crystal faces of the epitaxial ferroelectric film perpendicular to the Z crystal face is taken as an X crystal face, a face spacing of the X crystal face is
25 taken as x and a face spacing of the X crystal face of the material constituting the epitaxial ferroelectric film in a bulk state is taken as x_0 .

Still another object of the present invention is to provide a liquid discharge head for discharging a liquid, utilizing the aforementioned piezoelectric actuator. According to the present invention, there
5 can be obtained a piezoelectric actuator and a liquid discharge head, which are free from a film peeling or a deterioration of characteristics of the epitaxial ferroelectric film, shows excellent piezoelectric characteristics, is suitable for film formation and
10 miniaturization and for forming a large area.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a view showing an XRD pattern of a PZT thin film of a ferroelectric thin film element in
15 an example 1 of the present invention;

Fig. 2 is a view showing an electron diffraction image of the ferroelectric thin film element in the example 1 of the present invention;

Fig. 3 is a view showing an XRD pattern of an epitaxial ferroelectric film of a ferroelectric thin film element in an example 4 of the present invention;
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Fig. 4 is a view showing an electron diffraction image of the ferroelectric thin film element in the example 4 of the present invention;
25 and

Fig. 5 is a schematic cross-sectional view of

an ink jet head in an example 7 of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

5 A ferroelectric thin film element of the present invention has a structure including at least a substrate and an epitaxial ferroelectric thin film formed thereon. The epitaxial ferroelectric thin film formed on the substrate of the ferroelectric
10 thin film element of the present invention is a ferroelectric thin film having a single crystal structure or a crystal orientation property.

A piezoelectric actuator of the present invention has a structure including at least a
15 substrate, an epitaxial ferroelectric film formed thereon and electrodes formed on and under the epitaxial ferroelectric film. The epitaxial ferroelectric film formed on the substrate a ferroelectric film having a single crystal structure or a crystal orientation property, and electrodes are formed on and under, so as to sandwich the epitaxial ferroelectric film.

The epitaxial ferroelectric film of the present invention satisfies a relation $z/z_0 > 1.003$ wherein a
25 crystal face parallel to a crystal face of a surface of the substrate among crystal faces of the epitaxial ferroelectric film is taken as a Z crystal face, a

face spacing of the Z crystal face is taken as z and a spacing of the Z crystal face of a material constituting the epitaxial ferroelectric film in a bulk state is taken as z_0 . The epitaxial
5 ferroelectric film preferably satisfies a relation $z/z_0 > 1.004$, more preferably a relation $z/z_0 > 1.005$. In case the relation $z/z_0 > 1.003$ is satisfied, the spontaneous polarization of the epitaxial ferroelectric film can be increased even with such a
10 film thickness as 2 to 100 nm. Also in case such relation is satisfied, the epitaxial ferroelectric film can show a large spontaneous polarization even with a film thickness of 10 μm or less, thereby improving the piezoelectric characteristics.
15 A value of z/z_0 is not particularly restricted in the upper limit, but is generally 1.050 or less, preferably 1.020 or less and more preferably 1.010 or less. An upper limit value of z/z_0 selected as 1.050 or less allows to easily form an epitaxial film of a
20 satisfactory crystallinity.

Furthermore, the epitaxial ferroelectric film of the present invention satisfies a relation $0.997 \leq x/x_0 \leq 1.003$ wherein one of crystal faces of the epitaxial ferroelectric film perpendicular to the Z
25 crystal face is taken as an X crystal face, a face spacing of the X crystal face is taken as x and a face spacing of the X crystal face of the material

constituting the epitaxial ferroelectric film in a bulk state is taken as x_0 . The epitaxial ferroelectric film formed on the substrate of the ferroelectric film element of the present invention 5 preferably satisfies a relation $0.998 \leq x/x_0 \leq 1.002$, more preferably a relation $0.999 \leq x/x_0 \leq 1.001$. In case the aforementioned relation is satisfied, there can be obtained a ferroelectric thin film element which shows small stress applied in the epitaxial 10 ferroelectric film along a planar direction of the substrate, is free from a deterioration in the residual polarization or the fatigue resistance of the epitaxial ferroelectric film and is free from a film peeling. Also in case the aforementioned 15 relation is satisfied, there can be obtain a piezoelectric actuator which shows small stress applied to the epitaxial ferroelectric film along the planar direction of the substrate, and has excellent durability characteristics free from a deterioration 20 of the characteristics of the piezoelectric actuator in repeated use or a destruction of the epitaxial ferroelectric film associated with a leak current at a voltage application.

In the following there will be explained 25 specific embodiments of the present invention, required for realizing such ferroelectric element and piezoelectric actuator.

A material constituting the epitaxial ferroelectric film is not particularly restricted, and can be suitably selected from materials showing ferroelectricity. Examples of such material include

5 BaTiO₃, PbTiO₃, PbZrO₃, YMnO₃, Bi₄Ti₃O₁₂, SrBi₂Ta₂O₉, and (Sr, Ba)Nb₃. Examples of a material showing a strong ferroelectricity at the normal temperature are lead-based perovskite oxide materials generally represented by PZT. Also there can be employed a

10 composition in which the aforementioned main components are doped with a trace element such as La, for example La-doped PZT [(Pb, Ta)(Zr, Ti)O₃] (also represented as PLZT). In case of a piezoelectric actuator, there can be employed, as a material

15 showing a strong piezoelectric property, a relaxing ferroelectric member (relaxer) represented by lead niobate zincate-lead titanate (also represented as PZN-PT) or lead niobate magnesiate-lead titanate (also represented as PMN-PT).

20 A substrate usable in the preparation of the ferroelectric thin film element and the piezoelectric actuator of the present invention is preferably a single crystal member on which a ferroelectric film can be epitaxially grown. A preferred substrate is

25 for example a single crystal substrate such as of MgO, SrTiO₃, (La, Sr)TiO₃, Al₂O₃, Pt or Si. In particular, there is preferred SrTiO₃, (La, Sr)TiO₃,

MgO or Pt having a lattice constant close to that of a lead-based material which generally shows an excellent ferroelectric property, such as PZT. For example, a single crystal of SrTiO_3 , $(\text{La}, \text{Sr})\text{TiO}_3$, Pt 5 or MgO has a cubic crystal structure. Crystals of these materials in a bulk state have, at the room temperature, an a-axis lattice constant respectively of 3.905, 3.907, 3.923 and 4.211 Å. In case of forming, on a single crystal substrate prepared from 10 the above-mentioned material in such a manner that a (100) face constitutes the substrate surface, an epitaxial ferroelectric film having a tetragonal crystal structure in such a manner that a Z-crystal face of a PZT film constitutes a (001) face, a 15 material constituting the ferroelectric film is preferably PZT of a composition of $\text{Zr} : \text{Ti} = 52 : 48$, having a tetragonal crystal structure and an a-axis lattice constant of 4.306 Å in a bulk state at the room temperature.

20 It is also effective to provide a buffer layer between the substrate and the epitaxial ferroelectric film in order to obtain an epitaxial ferroelectric film of an excellent single crystal structure or an excellent crystal orientation property. A thickness 25 of the buffer layer is not particularly restricted, but it is usually 0.5 nm or larger, preferably 1 nm or larger and more preferably 2 nm or larger, since

it is preferable that the buffer layer has a high crystallinity.

In case of a ferroelectric element, the thickness is preferably such as not to hinder the characteristics thereof, and the thickness of the buffer layer is usually 100 nm or less, preferably 50 nm or less and more preferably 10 nm or less. For example, in case of forming an epitaxial ferroelectric thin film constituted of PZT on a Pt substrate, it is possible to obtain a epitaxial ferroelectric thin film of a better single-crystal quality by forming a PbTiO_3 layer of a thickness of 2 to 10 nm as a buffer layer and forming an epitaxial ferroelectric thin film on such buffer layer. This is presumably because the epitaxial growth of a single crystal can be controlled more easily in case Ti is richer than Zr in an initial growth stage of the epitaxial ferroelectric thin film constituted of PZT.

Also in case of a piezoelectric actuator, the thickness of the buffer layer is preferably such as not to hinder the characteristics thereof, and the thickness of the buffer layer is usually 1000 nm or less, preferably 500 nm or less and more preferably 100 nm or less. For example, in case of forming an epitaxial ferroelectric film constituted of PZT on a Pt substrate, it is possible to obtain a epitaxial

ferroelectric film of a better single-crystal quality by forming a PbTiO_3 layer of a thickness of 2 to 1000 nm as a buffer layer and forming an epitaxial ferroelectric film on such buffer layer. This is 5 presumably because the epitaxial growth of a single crystal can be controlled more easily in case Ti is richer than Zr in an initial growth stage of the epitaxial ferroelectric film constituted of PZT.

It is also effective to utilize a buffer layer 10 in order to obtain an epitaxial ferroelectric film having a single crystal structure or a crystal orientation property on a substrate prepared from a material such as Al_2O_3 or Si, having a large difference in the lattice constant from PZT. For 15 example it is possible to obtain an epitaxial ferroelectric film of a better single-crystal quality, on a substrate prepared on a Si(100) substrate by an epitaxial growth of yttria-stabilized zirconium oxide (also represented as YSZ) with a 20 (100) face thereof parallel to the substrate surface and by an epitaxial growth thereon of Pt(111), by forming an epitaxial ferroelectric film constituted of PZT(111) across a buffer layer constituted of PbTiO_3 . This is presumably because, with respect to 25 an a-axis lattice constant of YSZ of 5.16 Å, a crystal face (-110) perpendicular to the Pt(111) crystal face of the cubic crystal has a face spacing

of 5.55 Å, which is relatively close to the face spacing of the (100) face of YSZ.

- Also even on a substrate lacking orientation property such as stainless steel or glass, it is
- 5 possible to epitaxially grow a ferroelectric film having a single crystal structure or a crystal orientation property, utilizing a buffer layer. For example, since Pt has a property of spontaneous orientation in [111], a Pt film formed for example on
- 10 a glass substrate provides a high-orientation film having a (111) crystal face parallel to the substrate surface. It is possible to grow thereon an epitaxial ferroelectric film of PZT (111), across a buffer layer of TbTiO₃ (111).
- 15 As explained above, the buffer layer is useful means for obtaining an epitaxial ferroelectric film having a single crystal structure or a crystal orientation property.

- In case of utilizing an epitaxial ferroelectric
- 20 film in a memory medium such as a non-volatile memory, electrodes are required on and under the epitaxial ferroelectric film. Also a piezoelectric actuator has a structure including upper and lower electrodes sandwiching an epitaxial ferroelectric
- 25 film. Therefore, it is desirable that at least one of the substrate or the buffer layer constituting the ferroelectric thin film element or the piezoelectric

- actuator is electroconductive. As a material for the electrode, Pt or Au is ordinarily employed, but it is also possible to use Cr, Ru, Ir etc. or an oxide electrode material such as SrRuO₃ or (La, Sr)TiO₃.
- 5 There can also be employed an electrode material of multi-layered structure intended for a higher adhesion or an ohmic contact of the electrode, such as Pt/Ti. The conductive material employed for the electrode preferably has a specific resistivity of
- 10 0.01 Ω·cm or less.
- In the following, there will be shown specific examples of a layer structure of the ferroelectric thin film element and the piezoelectric actuator of the present invention.
- 15 The ferroelectric thin film element of the present invention has a structure including at least a substrate and an epitaxial ferroelectric thin film epitaxially formed on the substrate and having a single crystal structure or a crystal orientation
- 20 property, but, in an application for an electronic device such as a non-volatile memory, electrodes are often required on and under the epitaxial ferroelectric thin film. Therefore the configuration is represented by: upper electrode//ferroelectric
- 25 thin film//buffer layer//substrate; and a substrate or a buffer layer having conductivity is indicated by an underline. However this is not essential in case

the ferroelectric thin film element is applied to a device not necessarily requiring a conductive layer in the buffer layer, such as a ferroelectric gate transistor. Also, among these layers, at least the
5 epitaxial ferroelectric thin film is in an epitaxial relationship with an underlying film.

The piezoelectric actuator of the present invention has a structure including at least a substrate, an epitaxial ferroelectric film
10 epitaxially formed on the substrate and having a single crystal structure or a crystal orientation property, and electrodes positioned on and under so as to sandwich the epitaxial ferroelectric film. Therefore the specific layer configuration of the
15 piezoelectric actuator is represented in the following by: upper electrode//ferroelectric thin film//buffer layer//substrate, and a substrate or a buffer layer having conductivity and serving as an electrode is indicated by an underline. The
20 piezoelectric actuator of the present invention is particularly preferably applied to an actuator unit in a liquid discharge head. The piezoelectric actuator of the present invention particularly preferably has a configuration of employing, as the
25 substrate, a single crystal Si substrate bearing a SiO₂ layer formed by thermal oxidation of the substrate surface in which such substrate serves as a

vibrating plate. Among these layers on the substrate, at least the epitaxial ferroelectric film is in an epitaxial relationship with an underlying layer, having a crystalline property.

5 Ex. 1:

Pt//PZT(001)/PbTiO₃(001)//Pt(100)/MgO(100)//
Si(100)

Ex. 2:

Pt//PZT(001)/PbTiO₃(001)//Pt(100)/SrTiO₃(100)//
10 Si(100)

Ex. 3: Au//PZT(001)/(La, Sr)TiO₃(100)/
Si(100)/SiO₂//Si (100)

Ex. 4: Pt//PZT(001)/PbTiO₃(001)//Pt(100)//
Al₂O₃(100)//Si(100)

15 Ex. 5: Pt//PZT(111)/PbTiO₃(111)//Pt(111)//
YSZ(100)/Zr//Si(100)

Ex. 6: Ag//PZT(001)/PbTiO₃(001)//Pt(100)/
LaAlO₃(100)//Si(100)

Ex. 7: Au//PZT(001)/PbTiO₃(001)//Pt(100)//
20 YSZ(111)/SiO₂//Si(111)

Ex. 8: Au//PZT(001)//(La, Sr)TiO₃(100)//
YSZ(111)//Si(111)

Ex. 9: Pt//PZT(111)/PbTiO₃(111)//Pt(111)/
YSZ(100)//Si(100)

25 Ex. 10: Pt//PZT(111)//Pt(111)//glass

Ex. 11: Pt//PZT(111)//Pt (111)/MgO//SUS

Ex. 12: Pt//PZT(111)/PbTiO₃(111)//Pt(111)/

MgO(111)//Si(100)

Ex. 13: Au//PZT(001)//SrRuO₃(001)//Si(100)

Ex. 14: Au//PZT(001)/PbTiO₃(001)//Pt(100)//

MgO(100)

5 Ex. 15: Au//PZT(001)/PbTiO₃(001)//Pt(100)//
SrTiO(100)

Ex. 16: Pt//PZT(001)//(La, Sr)O₃(100)

Ex. 17: Au//PZT(001)/PbTiO₃(001)//Pt(100)//
Al₂O₃(100)

10 Ex. 18: Pt//PZT(001)//Ir(100)/ZrN(100)//Si(100)

Ex. 19: Pt//YMnO₃(0001)//Y₂O₃(111)//Si(111)

Ex. 20: Pt//PbZrO₃(101)//(La, Sr)O₃(100)

In the foregoing, there are principally shown examples employing PZT as the material constituting
15 the epitaxial ferroelectric film, but the material constituting the epitaxial ferroelectric film may be a composition doped with a trace element for example La, such as La-doped PZT. Also the material constituting the ferroelectric film may be not based
20 on lead but can also be a non-lead ferroelectric material such as BaTiO₃ or SrBi₂Ta₂O₉.

The ferroelectric thin film element of the present invention can be prepared by epitaxially forming a ferroelectric thin film on a substrate.
25 The piezoelectric actuator of the present invention can be prepared by epitaxially forming at least a ferroelectric film on a substrate and providing

electrodes on and under such epitaxial ferroelectric film. The piezoelectric actuator of the present invention has a structure including at least a substrate, an epitaxial ferroelectric film formed on 5 the substrate and having a single crystal structure or a crystal orientation property, and electrode films formed on and under the epitaxial ferroelectric film and having a crystal orientation property.

Such epitaxial ferroelectric film can be formed 10 for example by a sputtering method, a sol-gel method, a metalorganic chemical vapor deposition (also represented as MOCVD) method, an evaporation method, or a laser ablation method. Film forming conditions vary according to the film forming method and the 15 ferroelectric material to be employed, and can be suitably selected.

For example, in case of a sputtering method, an RF magnetron sputtering method is preferable. Film forming conditions in the RF magnetron sputtering 20 method include a substrate temperature at the film formation within a range from 500 to 700°C, an argon/oxygen atmosphere with an argon/oxygen ratio within a range from 20/1 to 50/1, a gas pressure from 0.2 Pa to 0.5 Pa, an RF charged electric power from 25 0.5 to 1.2 W/cm², and a substrate cooling rate after the film formation of 65°C/min. or higher. More preferred conditions include an argon/oxygen ratio

within a range from 30/1 to 50/1, a gas pressure from 0.2 Pa to 0.3 Pa, an RF charged electric power from 0.5 to 0.8 W/cm², and a substrate cooling rate after the film formation of 100°C/min. or higher. It is
5 particularly preferable to execute the cooling to 180°C with the above-mentioned speed, and it is also preferable to execute a pre-sputtering, prior to the film formation, briefly with a power equal to or less than a half of the RF charged electric power at the
10 film formation and to immediately proceed to the film formation. The film formation can be executed by suitably selecting conditions from those shown above, according to a desired composition of the epitaxial ferroelectric film. Particularly in a system
15 including a dopant such as La, it is possible to reduce the substrate temperature and to select a somewhat higher RF charge electric power. The heating of the substrate is preferably executed by infrared heating or resistor heating. In such case,
20 by maintaining a fluctuation of the substrate temperature within a range of ±5 %, it is possible to obtain an epitaxial ferroelectric film of uniform and stable characteristics even in case of forming an epitaxial ferroelectric film on a substrate of a
25 large area.

For forming the epitaxial ferroelectric film of the present invention, a sputtering method is

particularly preferable. This is because the sputtering method can easily provide an epitaxial ferroelectric film of satisfactory crystallinity having a crystal structure defined in the present

5 invention. For example, in case of a PZT(001) film epitaxially grown on a Pt(100) film, when a crystal orientation degree thereof becomes 90 % or higher, a ratio z/z_0 between a face spacing z of the (001) face present parallel to the substrate surface and

10 constituting the Z crystal face of the epitaxial ferroelectric film and a face spacing z_0 of the (001) face constituting the Z crystal face of PZT in a bulk state becomes larger than 1.003, and a ratio x/x_0 between a face spacing x of a (100) face present

15 perpendicularly to the Z crystal face and constituting the X crystal face of the epitaxial ferroelectric film and a face spacing x_0 of the (100) face constituting the X crystal face of PZT in a bulk state assumes a state $0.997 \leq x/x_0 \leq 1.003$. When the

20 crystal orientation degree further increases, the ratio x/x_0 of the face spacing of the (100) face in the epitaxial ferroelectric film and in the bulk state becomes closer to 1.

In the present invention, a crystal orientation degree means, in an X-ray measurement with an X-ray incident angle θ to the Z crystal face of the epitaxial ferroelectric film, a proportion of a

reflection peak intensity of all the Z faces of the epitaxial ferroelectric film to all the reflection peak intensities measured by a $2\theta/\theta$ method. For example in an epitaxial ferroelectric film having a
5 tetragonal (001) face crystal orientation, it means, in an X-ray diffraction pattern of the epitaxial ferroelectric film measured by the $2\theta/\theta$ method, a proportion of a sum of all the reflection peak intensities attributed to (00L) faces ($L = 1, 2,$
10 $3, \dots, n$) with respect to a sum of all the observed reflection peak intensities.

Also the epitaxial ferroelectric thin film of the ferroelectric thin film element of the present invention preferably has a thickness of 2 to 100 nm.
15 Since the ferroelectricity of an epitaxial ferroelectric film is developed depending on a skeleton of the crystal lattice and an atom arrangement, the film thickness is usually 2 nm or larger, preferably 5 nm or larger. On the other hand, in case of applying the ferroelectric thin film element of the present invention in a highly integrated device such as a ferroelectric memory,
20 since a thinner film of the epitaxial ferroelectric film is effective for such integration and for a low-voltage drive, the film thickness of the epitaxial ferroelectric thin film is preferably selected as 100 nm or less in case the application in such field is

intended.

In the piezoelectric actuator of the present invention, the epitaxial ferroelectric film preferably has a thinner thickness, particularly from 5 100 nm to 10 μm . For example incase a large piezoelectric displacement is required for the piezoelectric actuator, such as in a liquid discharge head for ink discharge, a smaller thickness of the epitaxial ferroelectric film allows to obtain a 10 larger displacement with a smaller voltage. In the piezoelectric actuator, however, the epitaxial ferroelectric film is subjected to a voltage application of several tens of volts, and, in order to prevent a destruction of the film by a variation 15 in such voltage or a deterioration of the piezoelectric characteristics by a leak current, the thickness of the epitaxial ferroelectric film is generally selected as 100 nm or larger, preferably 500 nm or larger. On the other hand, a larger 20 thickness of the epitaxial ferroelectric film increases of a frequency of defect generation such as a film peeling, and it becomes difficult to obtain an epitaxial ferroelectric film having single crystal structure or crystal orientation property, in all the 25 aforementioned ferroelectric materials, so that the thickness of the epitaxial ferroelectric film is preferably selected generally at 10 μm or less.

In the present invention, the epitaxial ferroelectric film is controlled in a crystal system and a face orientation thereof as explained in the following, thereby obtaining a ferroelectric film

5 without a deterioration in the characteristics, showing a large spontaneous polarization and suitable for a thin film formation. In an epitaxial ferroelectric film with a tetragonal crystal system, the epitaxial ferroelectric film has a spontaneous

10 polarization in a direction [001]. Therefore the spontaneous polarization becomes larger as a face spacing of the (001) face of the epitaxial ferroelectric film becomes longer than the face spacing of the (001) face in the bulk state.

15 Consequently, in a tetragonal crystal system, the Z crystal face is preferably (001) face.

On the other hand, in an epitaxial ferroelectric film with a rhombohedral crystal system, the epitaxial ferroelectric film has a spontaneous polarization in a direction [111].

20 Therefore the spontaneous polarization becomes larger as a face spacing of the (111) face of the ferroelectric film becomes longer than the face spacing of the (111) face in the bulk state.

25 Consequently, in the epitaxial ferroelectric film of a rhombohedral crystal system, the Z crystal face is preferably (111) face. Similarly in an epitaxial

ferroelectric film with a hexagonal crystal system, the epitaxial ferroelectric film has a spontaneous polarization in a direction [0001]. Therefore the spontaneous polarization becomes larger as a face
5 spacing of the (0001) face of the epitaxial ferroelectric film becomes longer than the face spacing of the (0001) face in the bulk state. Consequently, in the epitaxial ferroelectric film of a rhombohedral crystal system, the Z crystal face is
10 preferably (0001) face. Furthermore, in an epitaxial ferroelectric film with a rhombic crystal system, the epitaxial ferroelectric film has a spontaneous polarization in a direction [011]. Therefore the spontaneous polarization becomes larger as a face
15 spacing of the (011) face of the epitaxial ferroelectric film becomes longer than the face spacing of the (011) face in the bulk state. Consequently, in the epitaxial ferroelectric film of a rhombic crystal system, the Z crystal face is
20 preferably (011) face.

The hexagonal crystal system is represented not by the Miller's notation (hkl) utilized in the notation of crystal faces but by the Brave-Millar's notation (hikl) often employed in the hexagonal
25 system.

The liquid discharge head of the present invention is provided with a liquid discharge port, a

pressure chamber communicating with the liquid discharge port, a vibrating plate constituting a part of the pressure chamber, and a piezoelectric actuator unit provided outside the pressure chamber for
5 providing the vibrating plate with a vibration. The liquid discharge port generally has a shape of a nozzle. A part of the pressure chamber is constituted by the vibrating plate, and in an external part thereof at least the aforementioned
10 piezoelectric actuator is provided to constitute the ferroelectric actuator unit of the liquid discharge head.

In the liquid discharge head of such configuration, a predetermined voltage is applied to
15 the epitaxial ferroelectric film of the piezoelectric actuator to cause an extension-contraction motion of the epitaxial ferroelectric film having a piezoelectric property, thereby generating a bending vibration to change the volume of the pressure
20 chamber and to cause a pressure therein, whereby a liquid is supplied from a liquid supply unit and is discharged from the discharge port (also represented as nozzle). The discharge liquid can be various solutions or an ink.

25 In the liquid discharge head of the present invention, in case the nozzle for liquid discharge is present in plural units, the piezoelectric actuator

unit of the present invention generally has a structure basically divided for each nozzle. However there may be adopted a structure divided not for each nozzle but for each pressure chamber, or for every 5 several pitches. Also in case of dividing the piezoelectric actuator of the liquid discharge head of the present invention, it is not necessary to separate all the components from the substrate to the upper electrode but it is possible to separate the 10 epitaxial ferroelectric film and the upper electrode or the upper electrode alone.

Between the divided piezoelectric actuator units, a resin of a low rigidity or the like may be present as long as the extension-contraction motion 15 of each ferroelectric actuator is not hindered. The shape of the pressure chamber can be arbitrarily selected, such as rectangular, circular or oval. Also in case of a head which discharges liquid in a direction perpendicular to the longitudinal direction 20 of the pressure chamber, a cross-sectional shape of the pressure chamber may be so formed as to be contracted toward the nozzle.

Furthermore, in the liquid discharge head of the present invention, the piezoelectric actuator 25 unit may also be constructed by adjoining the ferroelectric actuator to the vibrating plate constituting a part of the pressure chamber, and, for

example, the vibrating plate may be constituted by the substrate itself of the piezoelectric actuator. In such case, the substrate preferably has properties having a crystal orientation, capable of epitaxially growing at least the lower electrode and the ferroelectric film, and also suitable as the vibrating plate. In such case, it is also possible to use, as the substrate, a substrate lacking the orientation property such as stainless steel or glass, on which a ferroelectric film having a single crystal structure or a crystal orientation property is epitaxially grown across a buffer layer. Also the liquid discharge head of the present invention may have a configuration including a piezoelectric actuator unit prepared by adhering a piezoelectric actuator of the present invention to the vibrating plate.

Also in the piezoelectric actuator or the liquid discharge head mentioned in the foregoing, in case a buffer layer is provided between the substrate and the epitaxial ferroelectric film and has a dielectric property, a thickness of the buffer layer is preferably made small since the piezoelectric displacement depends on an effective electric field applied to the epitaxial ferroelectric film having the piezoelectric property.

The piezoelectric actuator of the present

- invention shows excellent piezoelectric characteristics because of a large spontaneous polarization of the epitaxial ferroelectric film, also is free from a film peeling or a deterioration
- 5 in the characteristics of the epitaxial ferroelectric film because of a stress applied in the epitaxial ferroelectric film along the planar direction of the substrate, and can be easily made in a large area.
- Also the liquid discharge head of the present
- 10 invention, including the aforementioned piezoelectric actuator in the piezoelectric actuator unit, provides a large discharging power with a high density, also is excellent for a high frequency drive and is suitable for forming a large area.
- 15 Examples
- In the following, the ferroelectric thin film element of the present invention and the producing method thereof will be explained in detail by examples, with reference to accompanying drawings.
- 20 In the following examples and comparative examples, z/z_0 , x/x_0 and crystal orientation degree were adjusted by regulating film forming conditions of the epitaxial ferroelectric member (sputtering power, film forming temperature, cooling speed, sputtering
- 25 gas pressure, sputtering gas species, a target-substrate distance, target density etc.).

<Example 1>

On a substrate (single crystal growing substrate) ($\text{La}_{0.038}$, $\text{Sr}_{0.962}$) TiO_3 (100) serving also as an electrode, a PZT thin film of a thickness of 70 nm was epitaxially grown as an epitaxial ferroelectric 5 thin film by a sputtering apparatus of RF magnetron method, thereby obtaining a ferroelectric thin film element. In this operation, there were employed a substrate temperature of 600°C, an argon/oxygen ratio of 30/1 at the film formation, a gas pressure of 0.2 10 Pa, an RF power of 0.8 W/cm² at the film formation and a cooling speed after the film formation of 100°C/min until 180°C or lower is reached, and a pre-sputtering prior to the film formation was conducted for 3 minutes with an RF power of 0.3 W/cm². The PZT 15 thin film, constituting the epitaxial ferroelectric thin film, had a composition of $\text{Pb}(\text{Zr}_{0.52}, \text{Ti}_{0.48})\text{O}_3$. A single crystal property of the PZT thin film of thus prepared ferroelectric thin film element was measured by XRD. The obtained result is shown in Fig. 1.

20 Based on the result shown in Fig. 1, it was confirmed that the PZT thin film had a tetragonal crystal structure, a Z crystal face in (001) face and a crystal orientation degree of 100 %.

Also an electron beam diffraction was conducted 25 by introducing an electron beam from [010], which is perpendicular to a normal to the Z crystal face. The obtained result is shown in Fig. 2. Based on the

result shown in Fig. 2, it was confirmed that the PZT thin film had a single crystal structure of which a film growing face is (001).

Then a- and c-axis lattice constants were calculated from diffraction peaks of a (004) face of the PZT thin film, obtained in an XRD-2θ/θ measurement of a face of the PZT thin film horizontal to the substrate and from diffraction peaks of a (004) face of the PZT thin film, obtained in an XRT- $2\theta\chi/\phi$ measurement of a face of the PZT thin film perpendicular to the substrate. The measurement was conducted with an X-ray diffraction apparatus Rint-Inplane (trade name), manufactured by Rigaku Denki Co., with an X-ray output of 40 kV at 50 mA and with slits of 0.5° at a light receiving side and a detection side. As a result there were obtained $a = 4.041 \text{ \AA}$ and $c = 4.162 \text{ \AA}$. A reference (JCPDS-3320784) for a tetragonal bulk ceramics of PZT of a composition of Zr : Ti = 52 : 48 describes lattice constants $a_0 = 4.036 \text{ \AA}$ and $c_0 = 4.146 \text{ \AA}$, and $z/z_0 = c/c_0 = 1.0039$ and $x/x_0 = a/a_0 = 1.0012$.

On thus obtained ferroelectric thin film element, a Pt pattern of a diameter of 100 μm was formed by sputtering as an upper electrode, while a lower electrode was constituted of (La, St) TiO_3 and a ferroelectric property of the ferroelectric tin film element was evaluated by a Sawyer-Tower circuit. As

a result, there were obtained a spontaneous polarization $P_s = 100 \mu\text{C}/\text{cm}^2$ and a residual polarization $P_r = 45 \mu\text{C}/\text{cm}^2$. Also a fatigue characteristics test was conducted on 10 spots on the
5 piezoelectric Pt pattern of the ferroelectric thin film element. The evaluation was conducted under conditions of an applied voltage of $\pm 5 \text{ V}$, an evaluation temperature of 70°C , a frequency of 1 kHz and a writing of 10^7 times. As a result, a defective
10 element was not found in any of all the evaluated 10 spots. The obtained results are summarized in Table 1.

<Example 2>

On a substrate (single crystal growing
15 substrate) $(\text{La}_{0.038}, \text{Sr}_{0.962})\text{TiO}_3(100)$ serving also as an electrode, a PZT thin film of a thickness of 70 nm was epitaxially grown as an epitaxial ferroelectric thin film by a sputtering apparatus of RF magnetron method, thereby obtaining a ferroelectric thin film
20 element. In this operation, there were employed a substrate temperature of 600°C , an argon/oxygen ratio of 30/1 at the film formation, a gas pressure of 0.2 Pa, an RF power of $0.8 \text{ W}/\text{cm}^2$ at the film formation and a cooling speed after the film formation of
25 $80^\circ\text{C}/\text{min}$ until 180°C or lower is reached, and a pre-sputtering prior to the film formation was conducted for 30 minutes with an RF power of $0.3 \text{ W}/\text{cm}^2$. The PZT

thin film, constituting the epitaxial ferroelectric thin film, had a composition of $\text{Pb}(\text{Zr}_{0.52}, \text{Ti}_{0.48})\text{O}_3$. A single crystal property of the PZT thin film of thus prepared ferroelectric thin film element was measured
5 by XRD. The obtained result is shown in Fig. 1.

Based on the result shown in Fig. 1, it was confirmed that the PZT thin film had a tetragonal crystal structure, a Z crystal face in (001) face and a crystal orientation degree of 90 %.

10 Also an electron beam diffraction was conducted by introducing an electron beam from [010], which is perpendicular to a normal to the Z crystal face. As a result, it was confirmed that the PZT thin film had a single crystal structure of which a film growing
15 face is (001).

Then a- and c-axis lattice constants were calculated from diffraction peaks of a (004) face of the PZT thin film, obtained in an XRD- $2\theta/\theta$ measurement of a face of the PZT thin film horizontal
20 to the substrate and from diffraction peaks of a (004) face of the PZT thin film, obtained in an XRT- $2\theta\chi/\phi$ measurement of a face of the PZT thin film perpendicular to the substrate. As a result there were obtained $a = 4.034 \text{ \AA}$ and $c = 4.163 \text{ \AA}$, thus $z/z_0 = c/c_0 = 1.0042$ and $x/x_0 = a/a_0 = 0.9995$.
25

On thus obtained ferroelectric thin film element, a Pt pattern of a diameter of 100 μm was

formed by sputtering as an upper electrode, while a lower electrode was constituted of (La, St)TiO₃ and a ferroelectric property of the ferroelectric tin film element was evaluated. As a result, there were
5 obtained a spontaneous polarization $P_s = 90 \mu\text{C}/\text{cm}^2$ and a residual polarization $P_r = 40 \mu\text{C}/\text{cm}^2$. Also a fatigue characteristics test was conducted on 10 spots on the piezoelectric Pt pattern of the ferroelectric thin film element. As a result, a
10 defective element was not found in any of all the evaluated 10 spots. The obtained results are summarized in Table 1.

<Example 3>

A mirror polished Si(100) of 15 mm square was
15 employed as a substrate, and its surface was at first etched with tetramethylammonium hydroxide (also represented as TMAH) (manufactured by Kanto Chemical Co.) for 10 minutes at the room temperature, then washed with purified water and rinsed with an acetone vapor bath. Then, on this substrate, a YZT thin film
20 of a thickness of 10 nm was formed by a sputtering apparatus of RF magnetron method at a substrate temperature of 800°C. An XRD measurement after the film formation confirmed that the YSZ film had a
25 crystal orientation degree of 99 % or higher in a [100] direction. Then a Pt film was formed by 100 nm as a lower electrode by sputtering at a substrate

temperature of 600°C. An XRD measurement after the film formation confirmed that Pt had a crystal orientation degree of 97 % or higher in a [111] direction. Then, on these laminated films, a buffer 5 layer of $[\text{PbTiO}_3]$ (also represented as PT) was formed by 7 nm with a sputtering apparatus of RF magnetron method, with a substrate temperature of 600°C. An XRD measurement after the film formation confirmed that the PT had a crystal orientation degree of 94 % 10 or higher in a [111] direction. Then a PZT thin film was formed as an epitaxial ferroelectric thin film by 85 nm with a sputtering apparatus of RF magnetron type. In this operation, there were employed a substrate temperature of 600°C, an argon/oxygen ratio 15 of 30/1 at the film formation, a gas pressure of 0.2 Pa, an RF power of 0.8 W/cm² at the film formation and a cooling speed after the film formation of 100°C/min until 180°C or lower is reached, and a pre-sputtering prior to the film formation was conducted 20 for 3 minutes with an RF power of 0.3 W/cm². A single crystal property of the PZT thin film of thus prepared ferroelectric thin film element was measured by XRD. The obtained result is shown in Fig. 1. As a result, it was confirmed that the PZT thin film had 25 a rhombic crystal structure, a Z crystal face in (111) face and a crystal orientation degree of 92 %. The PZT thin film had a composition of

Pb_{(Zr_{0.58}Ti_{0.42})O₃}.

Then a face spacing of a (222) face, constituting Z crystal face of the rhombic PZT thin film and a face spacing of a (-220) face
5 perpendicular to the Z crystal face, were calculated from diffraction peaks of a (222) face of the PZT thin film, obtained in an XRD-2θ/θ measurement of a face of the PZT thin film horizontal to the substrate and from diffraction peaks of a (-220) face of the
10 PZT thin film, obtained in an XRT-2θχ/φ measurement of a face of the PZT thin film perpendicular to the substrate. As a result there were obtained $d_{(222)} = 1.186 \text{ \AA}$ and $d_{(-220)} = 1.433 \text{ \AA}$. A reference (JCPDS-732022) for a rhombic bulk ceramics of PZT of a
15 composition of Zr/Ti = 52/48 describes face spacings of $d_0_{(222)} = 1.1821 \text{ \AA}$ $d_0_{(-220)} = 1.4346 \text{ \AA}$, and $z/z_0 = d_{(222)}/d_0_{(222)} = 1.0035$ and $x/x_0 = d_{(-220)}/d_0_{(-220)} = 0.9987$.

On thus obtained ferroelectric thin film
20 element, a Pt pattern of a diameter of 100 μm was formed by sputtering as an upper electrode, while a lower electrode was constituted of Pt and a ferroelectric property of the ferroelectric tin film element was evaluated by a Sawyer-Tower circuit. As
25 a result, there were obtained a spontaneous polarization $P_s = 80 \mu\text{C/cm}^2$ and a residual polarization $P_r = 35 \mu\text{C/cm}^2$. Also a fatigue

characteristics test was conducted on 10 spots on the piezoelectric Pt pattern of the ferroelectric thin film element. The evaluation was conducted under conditions of an applied voltage of ± 5 V, an 5 evaluation temperature of 70°C, a frequency of 1 kHz and a writing of 10^7 times. As a result, a defective element was not found in any of all the evaluated 10 spots. The obtained results are summarized in Table 1.

10 <Comparative Examples 1 to 3>

Ferroelectric thin film elements were prepared by an epitaxial growth of a PZT thin film as an epitaxial ferroelectric thin film on a substrate with a sputtering apparatus of RF magnetron method, 15 and by adjusting z/z_0 , x/x_0 and crystal orientation degree through regulations of the film forming conditions in the same manner as in Example 1 except that the cooling speed after the film formation was not controlled below 400°C and that the pre- 20 sputtering was conducted for 60 minutes with an RF power same as in the film formation. Obtained results are shown in Table 1.

Table 1

	z/z_0	x/x_0	crystal orientation degree (%)	P_s ($\mu\text{C}/\text{cm}^2$)	P_s ($\mu\text{C}/\text{cm}^2$)	fatigue property (defect/all)
Ex. 1	1.0039	1.0012	100	100	45	0/10
Ex. 2	1.0042	0.9995	90	90	40	0/10
Ex. 3	1.0035	0.9987	92	80	35	0/10
Comp. Ex. 1	1.0005	1.0022	95	70	28	0/10
Comp. Ex. 2	1.0061	0.9922	99	100	35	5/10
Comp. Ex. 3	1.0036	0.9968	80	75	30	3/10

Results shown in Table 1 indicate that, in all the ferroelectric thin film elements of the examples 1 to 3 of the present invention, the epitaxial ferroelectric thin film satisfied relations of $z/z_0 > 5$ 1.003 and $0.997 \leq x/x_0 \leq 1.003$. Also the epitaxial ferroelectric thin film of the ferroelectric thin film elements of the examples had a crystal orientation degree of 90 % or higher, a spontaneous polarization P_s of $80 \mu\text{C}/\text{cm}^2$ or higher and a residual polarization P_r of $35 \mu\text{C}/\text{cm}^2$. Also the ferroelectric thin film elements passed fatigue test of 10^7 times.

On the other hand, in the ferroelectric thin film element of the comparative example 1, the epitaxial ferroelectric thin film showed a relation $15 z/z_0 \leq 1.003$, and this ferroelectric thin film element cleared the fatigue test of 10^7 times but shows low ferroelectricity with a spontaneous polarization P_s of $70 \mu\text{C}/\text{cm}^2$ and a residual polarization P_r of $28 \mu\text{C}/\text{cm}^2$. In the ferroelectric thin film element of the comparative example 2, the epitaxial ferroelectric thin film showed a relation $20 z/z_0 < 0.997$, and this ferroelectric thin film element, though showing a strong ferroelectricity, was unable to clear the fatigue test of 10^7 times in some cases. Also in the ferroelectric thin film element of the comparative example 3, the epitaxial ferroelectric thin film showed a relation $25 z/z_0 <$

0.997, a crystal orientation degree less than 90 % and a low ferroelectricity with a spontaneous polarization P_s of $75 \mu\text{C}/\text{cm}^2$ and a residual polarization P_r of $30 \mu\text{C}/\text{cm}^2$, and was unable to clear 5 the fatigue test of 10^7 times in some cases.

In the following, the piezoelectric actuator and the liquid discharge head of the present invention and the producing method thereof will be explained in detail by examples, with reference to 10 accompanying drawings. In the following examples and comparative examples, z/z_0 , x/x_0 and crystal orientation degree were adjusted by regulating film forming conditions of the epitaxial ferroelectric member (sputtering power, film forming temperature, 15 cooling speed, sputtering gas pressure, sputtering gas species, a target-substrate distance, target density etc.). In the examples, explanation will be made on a liquid discharge head and an ink jet head as examples.

20 <Example 4>

On a substrate (single crystal growing substrate) $(\text{La}_{0.038}, \text{Sr}_{0.962})\text{TiO}_3$ (100) serving also as an electrode, a PZT thin film of a thickness of $2 \mu\text{m}$ was epitaxially grown as an epitaxial ferroelectric 25 film by a sputtering apparatus of RF magnetron type. In this operation, there were employed a substrate temperature of 600°C , an argon/oxygen ratio of 30/1

at the film formation, a gas pressure of 0.2 Pa, an RF power of 0.8 W/cm² at the film formation and a cooling speed after the film formation of 100°C/min until 180°C or lower is reached, and a pre-sputtering 5 prior to the film formation was conducted for 3 minutes with an RF power of 0.3 W/cm². The PZT film had a composition of Pb(Zr_{0.52}, Ti_{0.48})O₃. A single crystal property of thus prepared epitaxial ferroelectric film was measured by XRD. The obtained 10 result is shown in Fig. 1. Based on the result shown in Fig. 1, it was confirmed that the PZT thin film had a tetragonal crystal structure, a Z crystal face in (001) face and a crystal orientation degree of 100 %.

15 Also an electron beam diffraction was conducted by introducing an electron beam from [010], which is perpendicular to a normal to the Z crystal face. The obtained result is shown in Fig. 2. Based on the result shown in Fig. 2, it was confirmed that the PZT 20 film had a single crystal structure of which a film growing face is (001).

Then a- and c-axis lattice constants were calculated from diffraction peaks of a (004) face of the PZT film, obtained in an XRD-2θ/θ measurement of 25 a face of the PZT film horizontal to the substrate and from diffraction peaks of a (004) face of the PZT film, obtained in an XRT-2θχ/φ measurement of a face

of the PZT film perpendicular to the substrate. The measurement was conducted with an X-ray diffraction apparatus Rint-Inplane (trade name), manufactured by Rigaku Denki Co., with an X-ray output of 40 kV at 50 mA and with slits of 0.5° at a light receiving side and a detection side. As a result there were obtained $a = 4.042 \text{ \AA}$ and $c = 4.171 \text{ \AA}$. A reference (JCPDS-3320784) for a tetragonal bulk ceramics of PZT of a composition of Zr : Ti = 52 : 48 describes lattice constants $a_0 = 4.036 \text{ \AA}$ and $c_0 = 4.146 \text{ \AA}$, and $z/z_0 = c/c_0 = 1.0060$ and $x/x_0 = a/a_0 = 1.0015$.

On thus obtained ferroelectric thin film element, a Pt pattern of a diameter of 100 μm was formed by sputtering as an upper electrode, thereby preparing a piezoelectric actuator with a lower electrode of $(\text{La}, \text{St})\text{TiO}_3$. Such piezoelectric actuator was subjected to a measurement of a piezoelectric constant d_{33} with a piezoelectric constant measurement apparatus (manufactured by Toyo Technica Co.). There was obtained a result $d_{33} = 498 \text{ pC/N}$.

Also for the purpose of evaluating a displacement amount of such piezoelectric actuator, there was prepared a piezoelectric actuator in which an LSTO substrate also serves as a vibrating plate.

At first a substrate (single crystal growing substrate) $(\text{La}_{0.038}, \text{Sr}_{0.962})\text{TiO}_3$ (100) serving also as

an electrode (also represented as LSTO substrate) was adjoined to a Si (100) substrate, and a side of the LSTO substrate was ground until the LSTO reached a thickness of about 5 μm . Then a PZT film was formed
5 as an epitaxial ferroelectric film by 3.0 μm , and a Pt electrode pattern was formed thereon by sputtering. Then the Si substrate was etched with a pattern of a length of 600 μm and a width of 40 μm by a dry etching processing, thereby preparing a
10 cantilever of unimorph type in which the LSTO substrate constitutes a vibrating plate. The upper electrode was patterned in a length of 600 μm and a width of 40 μm as in the cantilever. A displacement amount of thus prepared unimorph cantilever was
15 measured with a laser Doppler measuring device, and was confirmed as 50 nm under a voltage application of 10 V.

A durability test was conducted on this piezoelectric actuator under conditions of an applied
20 voltage of ± 20 V, an evaluation temperature of 70°C, a frequency of 1 kHz and a writing of 10^7 times. As a result, there was not observed an attenuation of the displacement by a deterioration or a peeling of the film.

25 Results of the durability test for the piezoelectric actuator were evaluated according to following criteria:

+: displacement amount after durability test was larger than 70 % of the displacement amount prior to the durability test;

-: displacement amount after durability test was 5 equal to or less than 70 % of the displacement amount prior to the durability test.

The obtained results are summarized in Table 2.

<Example 5>

On a substrate (single crystal growing
10 substrate) ($\text{La}_{0.038}$, $\text{Sr}_{0.962}$) TiO_3 (100) serving also as an electrode, a PZT thin film of a thickness of 3.0 μm was epitaxially grown as an epitaxial ferroelectric film by a sputtering apparatus of RF magnetron type. In this operation, there were
15 employed a substrate temperature of 600°C, an argon/oxygen ratio of 30/1 at the film formation, a gas pressure of 0.2 Pa, an RF power of 0.8 W/cm² at the film formation and a cooling speed after the film formation of 80°C/min until 180°C or lower is
20 reached, and a pre-sputtering prior to the film formation was conducted for 3 minutes with an RF power of 0.3 W/cm². The PZT film had a composition of $\text{Pb}(\text{Zr}_{0.52}, \text{Ti}_{0.48})\text{O}_3$. A single crystal property of thus prepared epitaxial ferroelectric film was measured by
25 XRD. The obtained result is shown in Fig. 1. Based on the result shown in Fig. 1, it was confirmed that the PZT thin film had a tetragonal crystal structure,

a Z crystal face in (001) face and a crystal orientation degree of 90 %.

Also an electron beam diffraction was conducted by introducing an electron beam from [010], which is 5 perpendicular to a normal to the Z crystal face.

Based on the result, it was confirmed that the PZT film had a single crystal structure of which a film growing face is (001).

Then a- and c-axis lattice constants were 10 calculated from diffraction peaks of a (004) face of the PZT film, obtained in an XRD- $2\theta/\theta$ measurement of a face of the PZT film horizontal to the substrate and from diffraction peaks of a (004) face of the PZT film, obtained in an XRT- $2\theta\chi/\phi$ measurement of a face 15 of the PZT film perpendicular to the substrate. As a result there were obtained $a = 4.033 \text{ \AA}$ and $c = 4.162 \text{ \AA}$, with $z/z_0 = c/c_0 = 1.0039$ and $x/x_0 = a/a_0 = 0.9993$.

On thus obtained ferroelectric thin film element, a Pt pattern of a diameter of $100 \mu\text{m}$ was 20 formed by sputtering as an upper electrode, thereby preparing a piezoelectric actuator with a lower electrode of $(\text{La}, \text{St})\text{TiO}_3$. Such piezoelectric actuator was subjected to a measurement of a piezoelectric constant d_{33} as in Example 4. There 25 was obtained a result $d_{33} = 450 \text{ pC/N}$.

Also for the purpose of evaluating a displacement amount of such piezoelectric actuator,

there was prepared a piezoelectric actuator in which an LSTO substrate also serves as a vibrating plate.

At first a substrate (single crystal growing substrate) ($\text{La}_{0.038}$, $\text{Sr}_{0.962}$) TiO_3 (100) serving also as
5 an electrode (also represented as LSTO substrate) was adjoined to a Si (100) substrate, and a side of the LSTO substrate was ground until the LSTO reached a thickness of about 5 μm . Then a PZT film was formed as an epitaxial ferroelectric film by 3.0 μm , and a
10 Pt electrode pattern was formed thereon by sputtering. Then the Si substrate was etched with a pattern of a length of 600 μm and a width of 40 μm by a dry etching processing, thereby preparing a cantilever of unimorph type in which the LSTO
15 substrate constitutes a vibrating plate. The upper electrode was patterned in a length of 600 μm and a width of 40 μm as in the cantilever. A displacement amount of thus prepared unimorph cantilever was measured with a laser Doppler measuring device, and
20 was confirmed as 46 nm under a voltage application of 10 V.

A durability test was conducted on this piezoelectric actuator under conditions of an applied voltage of ± 20 V, an evaluation temperature of 70°C,
25 a frequency of 1 kHz and a writing of 10^7 times. As a result, there was not observed an attenuation of the displacement by a deterioration or a peeling of the

film. The obtained results are summarized in Table 2.

<Example 6>

A mirror polished Si (100) was employed as a substrate, and its surface was at first etched with tetramethylammonium hydroxide (also represented as TMAH) (manufactured by Kanto Chemical Co.) for 10 minutes at the room temperature, then washed with purified water and rinsed with an acetone vapor bath. Then, on this substrate, a YZT film of a thickness of 10 nm was formed by a sputtering apparatus of RF magnetron method at a substrate temperature of 800°C. An XRD measurement after the film formation confirmed that the YSZ film had a crystal orientation degree of 99 % or higher in a [100] direction.

Then a Pt film was formed by 100 nm as a lower electrode by sputtering at a substrate temperature of 600°C. An XRD measurement after the film formation confirmed that Pt had a crystal orientation degree of 97 % or higher in a [111] direction. Then, on these laminated films, a buffer layer of $[PbTiO_3]$ (also represented as PT) was formed by 7 nm with a sputtering apparatus of RF magnetron method, with a substrate temperature of 600°C. An XRD measurement after the film formation confirmed that the PT had a crystal orientation degree of 94 % or higher in a [111] direction.

Then a PZT thin film was formed as an epitaxial ferroelectric thin film by 3.0 μm with a sputtering apparatus of RF magnetron type. In this operation, there were employed a substrate temperature of 600°C,
5 an argon/oxygen ratio of 30/1 at the film formation, a gas pressure of 0.2 Pa, an RF power of 0.8 W/cm² at the film formation and a cooling speed after the film formation of 100°C/min until 180°C or lower is reached, and a pre-sputtering prior to the film
10 formation was conducted for 3 minutes with an RF power of 0.3 W/cm². A single crystal property of thus prepared epitaxial ferroelectric film was measured by XRD. As a result, it was confirmed that the PZT film had a rhombic crystal structure, a Z crystal face in
15 (111) face and a crystal orientation degree of 92 %. The PZT thin film had a composition of
 $\text{Pb}(\text{Zr}_{0.58}\text{Ti}_{0.42})\text{O}_3$.

Then a face spacing of a (222) face, constituting Z crystal face of the rhombic PZT film
20 and a face spacing of a (-220) face perpendicular to the Z crystal face, were calculated from diffraction peaks of a (222) face of the PZT film, obtained in an XRD-2θ/θ measurement of a face of the PZT film horizontal to the substrate and from diffraction peaks of a (-220) face of the PZT film, obtained in
25 an XRT-2θχ/φ measurement of a face of the PZT film perpendicular to the substrate. As a result there

were obtained $d(222) = 1.187 \text{ \AA}$ and $d(-220) = 1.432 \text{ \AA}$. A reference (JCPDS-732022) for a rhombic bulk ceramics of PZT of a composition of Zr/Ti = 52/48 describes face spacings of $d_0(222) = 1.1821 \text{ \AA}$, $d_0(-220) = 1.4346 \text{ \AA}$, and $z/z_0 = d(222)/d_0(222) = 1.0041$ and $x/x_0 = d(-220)/d_0(-220) = 0.9982$.

On thus obtained ferroelectric thin film element, a Pt pattern of a diameter of 100 μm was formed by sputtering as an upper electrode, and a piezoelectric actuator was thus prepared with a lower electrode of $(\text{La}, \text{Sr})\text{O}_3$. Such piezoelectric actuator was subjected to a measurement of a piezoelectric constant d_{33} with a piezoelectric constant measurement apparatus (manufactured by Toyo Technica Co.). There was obtained a result $d_{33} = 471 \text{ pC/N}$.

Also for the purpose of evaluating a displacement amount of such piezoelectric actuator, there was prepared a cantilever of a unimorph type, in which the Si substrate constitutes a vibrating plate, by etching the Si substrate to a thickness of about 5 μm by a dry process in a range of a length of 600 μm and a width of 40 μm . A displacement amount of thus prepared unimorph cantilever was measured with a laser Doppler measuring device, and was confirmed as 46 nm under a voltage application of 10 V.

A durability test was conducted on this

piezoelectric actuator under conditions of an applied voltage of ± 20 V, an evaluation temperature of 70°C , a frequency of 1 kHz and a writing of 10^7 times. As a result, there was not observed an attenuation of the
5 displacement by a deterioration or a peeling of the film. The obtained results are summarized in Table 2.

<Example 7>

Fig. 3 shows a schematic cross-sectional view
10 of an ink jet head of the present example. A substrate having a configuration of boron (B)-doped monocrystalline Si (100)/ SiO_2 /Si (layer thicknesses of $2.5\ \mu\text{m}/1\ \mu\text{m}/250\ \mu\text{m}$ was employed, and a MgO (100) film was formed with a thickness of $0.3\ \mu\text{m}$ on the Si
15 (100) layer. Then a Pt (001) film of $0.2\ \mu\text{m}$ as an electrode, a PT (001) film of $0.1\ \mu\text{m}$ thereon, and a PZT film of a thickness of $2\ \mu\text{m}$ prepared under same conditions as in the example 4 as an epitaxial ferroelectric film having a piezoelectric property
20 were prepared in succession by epitaxial growing. The PZT film had a composition of $\text{Pb}(\text{Zr}_{0.52}, \text{Ti}_{0.48})\text{O}_3$. Then an Au paste was coated as an upper electrode whereby a piezoelectric actuator unit was prepared.

The aforementioned Si layer was subjected to a
25 plasma etching with SF_6 and C_4F_8 to form a pressure chamber. Then an ink jet head shown in Fig. 3 was prepared by adjoining the Si substrate constituting a

part of the pressure chamber and a nozzle plate. The pressure chamber had a width of 60 μm and a depth of 2.2 mm, and a partition of the pressure chambers had a width of 24 μm .

5 Then a- and c-axis lattice constants were calculated from diffraction peaks of a (004) face of the PZT film, obtained in an XRD- $2\theta/\theta$ measurement of a face of the PZT film of the piezoelectric actuator horizontal to the substrate and from diffraction
10 peaks of a (004) face of the PZT film, obtained in an XRT- $20\chi/\phi$ measurement of a face of the PZT film perpendicular to the substrate. As a result there were obtained $a = 4.040 \text{ \AA}$ and $c = 4.165 \text{ \AA}$, with $z/z_0 = c/c_0 = 1.0045$ and $x/x_0 = a/a_0 = 1.0010$. An XRD
15 measurement of the single crystal property confirmed that the PZT film had a tetragonal crystal structure, a Z crystal face in (001) face and a crystal orientation degree of 99 %.

20 In an ink discharge from a nozzle in such ink jet head, a stable ink discharge could be confirmed even with a drive frequency of 10 kHz and a drive voltage of 3 V. Also a durability test of the ink jet nozzle was conducted with a drive frequency of 1 kHz and a drive voltage of 0 V/30 V. As a result,
25 the ink discharge was achieved in all the nozzles, and there has not been observed a film peeling or a deterioration in the characteristics of the epitaxial

ferroelectric film even after the durability test.

<Comparative Examples 4 to 6>

Piezoelectric actuators were prepared by an epitaxial growth of a PZT film as an epitaxial 5 ferroelectric film on a substrate with a sputtering apparatus of RF magnetron method, in which z/z_0 , x/x_0 and crystal orientation degree were adjusted through regulations of the film forming conditions in the same manner as in Example 5 except that the cooling 10 speed after the film formation was not controlled below 400°C and that the pre-sputtering was conducted for 60 minutes with an RF power same as in the film formation. Obtained results are shown in Table 1.

It was confirmed that the PZT films of the 15 comparative examples 4 to 6 were tetragonal crystals and the Z crystal face was a (001) face. Table 2 also shows z/z_0 and x/x_0 of the PZT film, piezoelectric constant d33 and the displacement amount of the piezoelectric actuator and an 20 evaluation result of the piezoelectric actuator in the durability test. The piezoelectric actuator of the comparative example 4 did not show satisfactory values in the piezoelectric constant d33 and the displacement amount of the piezoelectric actuator. 25 Also the piezoelectric actuator of the comparative example 5 could not clear 10^7 cycles, and was confirmed to show a reduction in the displacement

amount. Also the piezoelectric actuator of the comparative example 6 could not clear 10^7 cycles, and was confirmed to show a reduction in the displacement amount.

5 <Comparative Example 7>

As a comparative example of the example 7, an ink jet head of a following configuration was prepared. A substrate having a configuration of boron (B)-doped monocrystalline Si (100)/SiO₂/Si
10 (layer thicknesses of 2.5 μm/1 μm/250 μm was employed, and a MgO (100) film was formed with a thickness of 0.3 μm on the Si (100) layer. Then a Pt (001) film of 0.2 μm as an electrode, a PT (001) film of 0.1 μm thereon, and a PZT film of a thickness of 2
15 μm prepared under same conditions as in the example 4 as an epitaxial ferroelectric film having a piezoelectric property were prepared in succession by epitaxial growing. The PZT film had a composition of Pb(Zr_{0.52}, Ti_{0.48})O₃. Then an Au paste was coated as an
20 upper electrode whereby a piezoelectric actuator unit was prepared.

The aforementioned Si layer was subjected to a plasma etching with SF₆ and C₄F₈ to form a pressure chamber. Then an ink jet head similar to that in the
25 example 7 was prepared by adjoining the Si substrate constituting a part of the pressure chamber and a nozzle plate. The pressure chamber had a width of 60

μm and a depth of 2.2 mm, and a partition of the pressure chambers had a width of 24 μm .

Then a- and c-axis lattice constants were calculated from diffraction peaks of a (004) face of the PZT film, obtained in an XRD- $2\theta/\theta$ measurement of a face of the PZT film of the piezoelectric actuator horizontal to the substrate and from diffraction peaks of a (004) face of the PZT film, obtained in an XRT- $2\theta\chi/\phi$ measurement of a face of the PZT film perpendicular to the substrate. As a result there were obtained $a = 4.012 \text{ \AA}$ and $c = 4.151 \text{ \AA}$, with $z/z_0 = c/c_0 = 1.0012$ and $x/x_0 = a/a_0 = 0.9940$. An XRD measurement of the single crystal property confirmed that the PZT had a tetragonal crystal structure, a Z crystal face in (001) face and a crystal orientation degree of 78 %.

In an ink discharge from a nozzle in such ink jet head, a stable ink discharge could be confirmed even with a drive frequency of 10 kHz and a drive voltage of 7 V, but an ink discharge could not observed at a drive frequency of 10 kHz and a drive voltage of 3 V. Also in a durability test of the ink jet nozzle conducted with a drive frequency of 1 kHz and a drive voltage of 0 V/30 V, there was observed an ink discharge failure in plural nozzles in the discharge to 10^7 cycles.

Table 2

	z/z_0	x/x_0	crystal orientation degree	d_{33} (pC/N)	displace- ment amount (nm)	piezoelectric actuator durability test
Ex. 4	1.0060	1.0015	100	498	50	+
Ex. 5	1.0039	0.9993	90	450	46	+
Ex. 6	1.0041	0.9982	92	471	46	+
Comp.Ex.4	1.0007	1.0019	95	347	28	+
Comp.Ex.5	1.0068	0.9895	99	505	45	-
Comp.Ex.6	1.0038	0.9958	80	375	36	-

Based on the results shown in Table 2 and explained above, in the piezoelectric actuators of the examples 4 to 6 and the ink jet head of the example 7, the epitaxial ferroelectric thin film satisfied relations of $z/z_0 > 1.003$ and $0.997 \leq x/x_0 \leq 1.003$. Also the crystal orientation degree was 90 % or higher. Also the piezoelectric actuators of the examples 4 to 6 had a piezoelectric constant d_{33} of 450 pC/N or higher, and a displacement amount of 46 nm or higher. Also the piezoelectric actuators of the examples 4 to 6 did not show, in a durability test, an attenuation in the displacement amount by a deterioration or a peeling of the ferroelectric film in the piezoelectric actuator unit. Also as explained above, the ink jet head of the example 7 did not show, after the fatigue test of 10^7 times, a film peeling of the epitaxial ferroelectric film in the piezoelectric actuator unit or a defective discharge.

On the other hand, in the epitaxial ferroelectric film of the piezoelectric actuator of comparative example 4, the epitaxial ferroelectric thin film showed a relation $z/z_0 < 1.003$, and the piezoelectric actuator of the comparative example 4 showed a low piezoelectric property with a piezoelectric constant d_{33} of 347 pC/N and a displacement amount of 28 nm.

In the piezoelectric actuator of the

comparative example 5, the epitaxial ferroelectric film showed a relation $z/z_0 > 1.003$. Therefore the piezoelectric actuator of the comparative example 5 showed a strong piezoelectric property with a

5 piezoelectric constant d_{33} of 505 pC/N and a displacement amount of 45 nm, as in the examples, but, because of a relation $x/x_0 < 0.997$, the piezoelectric actuator of the comparative example 5 could not clear the fatigue test of 10^7 times.

10 In the piezoelectric actuator of the comparative example 6, the epitaxial ferroelectric film showed a relation $z/z_0 < 0.997$, and a crystal orientation degree of (001) face of the PZT film as low as 80 %. Also the piezoelectric actuator of the
15 comparative example 6 had a low piezoelectric property with a piezoelectric constant d_{33} of 375 pC/N and a displacement amount of 36 nm, could not clear the fatigue test of 10^7 times, thus indicating a reduction in the displacement amount.